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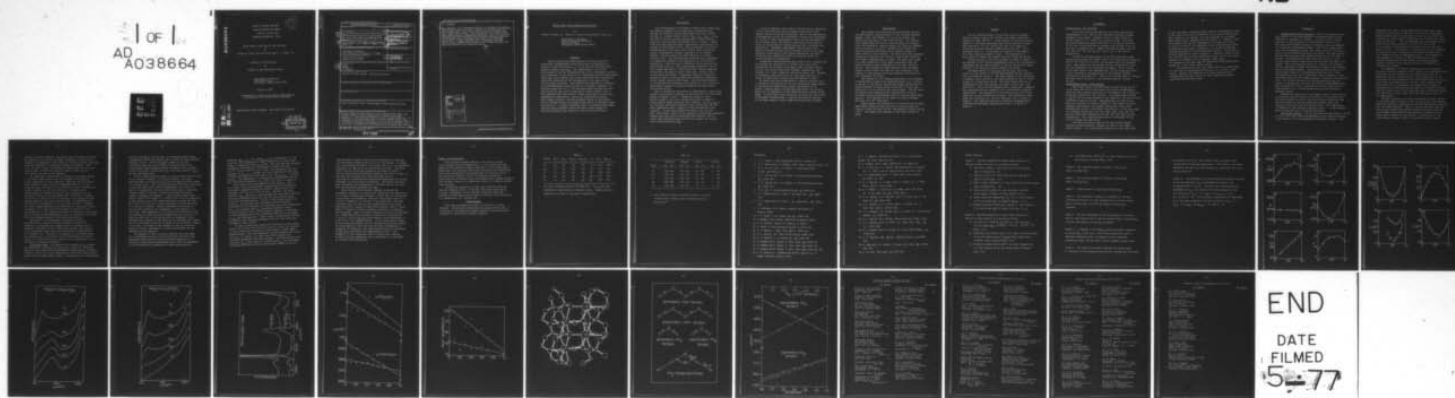
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Mixed Alkali Glass Spectra and Structure

by

George B. Rouse, Phillip Miller and W. M. Risen, Jr.

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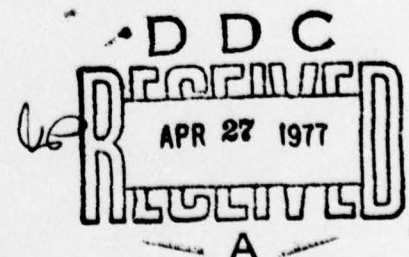
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## Mixed Alkali Glass Spectra and Structure

by

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### Abstract

The far infrared and Raman spectra of several series of mixed alkali metaphosphate glasses have been investigated as a function of the mole fraction,  $x$ , of the network modifying ionic oxides in  $xM_2O(1-x)M'_2O \cdot P_2O_5$ . The frequencies of the cation-motion bands in the far infrared spectra, which correspond to cation-site vibrations, do not shift with  $x$ , indicating that the vibrationally significant local geometry and forces associated with a particular cation are unaffected by the introduction of the second cation into the glass structure. Each Raman-active band due to vibrations of the metaphosphate network occurs at a different frequency for each pure glass ( $x=0$  or  $1$ ), but for mixed alkali glasses only one band occurs for each type of mode and it varies linearly with  $x$ . This indicates that the cations in these mixed alkali glasses are homogeneously distributed, there is no significant molecular-level domain formation, and the phosphate chains are associated with an averaged cation environment whose effect on the chain modes varies with  $x$ . A simple vibrational model is presented which shows that the cation-dependent shifts are due to small changes in network bond angles and variation of the cation-site forces.

## Introduction

Ionic oxide glasses of the general formula  $xM_2O(1-x)M'_2O \cdot yA_{p/q}O_q$  are commonly referred to as mixed alkali glasses when  $M_2O$  and  $M'_2O$  are different network modifying alkali metal oxides and  $A_{p/q}O_q$  is a network former such as  $SiO_2$ ,  $P_2O_5$ ,  $B_2O_3$ , or  $GeO_2$ . They are of special interest because many of their physical properties vary extremely nonlinearly as  $x$  is varied. Indeed, there have been many systematic experimental investigations of glasses in mixed alkali series, made by changing the relative concentrations of the alkali metal oxides while holding the overall stoichiometry constant (varying  $x$  in the general formula), and the results have been discussed in several articles (1-8). The nonlinearities found are most pronounced for properties related to ionic mobility such as electrical conductivity, ionic diffusion, dielectric relaxation and loss, and internal friction. Bulk thermodynamic properties such as molar volume and density, refractive index, thermal expansion coefficient, and elastic moduli either vary linearly with  $x$  or show small deviations. Properties related to structural relaxation such as viscosity and glass transition temperature usually exhibit negative deviations. This nonlinear behavior of certain physical properties with respect to  $x$  in a series of mixed alkali glasses is generally known as the mixed alkali (polycation) effect.

Some of the physical properties of representative ionic oxide glasses are plotted as functions of mole fraction of a particular cation in Figures 1 and 2. Properties related to ionic mobility (such as the ionic conductivity shown in Figure 2) always exhibit large deviations from linearity, and the plots of log viscosity and glass temperature show a deviation, but the other properties shown in Figure 1 do not deviate much from linearity. It has been suggested by Shelby (14) that the term "mixed alkali effect" not be applied to these other properties because they show similar deviations from linearity even in binary glass forming systems which do not contain any cations, such as the system  $GeO_2-SiO_2$ .

As may be expected, while most of the theoretical approaches (15-24) that have been taken to explain these mixed alkali effects involve microscopic mechanisms, most of the experimental investigations involve the measurement of macroscopic properties. So, little is known experimentally about relevant interactions on the atomic scale, particularly those that involve cation-cation or cation-network interactions and their variation with composition. Systematic experimental studies which yield specific information about the microscopic nature of the glass structure (particularly these cation interactions) and their variations with composition would be extremely useful for future theoretical explanations.

Vibrational spectroscopy has been shown to be a valuable tool for probing the interactions of cations with their local environments in solution, in polymers, and in glasses (25-28). In fact, the cation vibrational frequency observed has been related to the ionic conduction activation energy (29). However, no systematic investigation of the vibrational spectra of a series of mixed alkali glasses has been reported to date.

We report here some observations of interest obtained from a systematic investigation of the far infrared and Raman spectra of two series of mixed alkali glasses represented by the general formulae  $x\text{Rb}_2\text{O} \cdot (1-x)\text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5$  and  $x\text{Rb}_2\text{O} \cdot (1-x)\text{Li}_2\text{O} \cdot \text{P}_2\text{O}_5$ , which will be referred to as the Rb-Na and Rb-Li glasses in the paper. We also report some vibrational calculations which offer a reasonable interpretation of some of the observed features in the Raman spectra of both single and mixed alkali glasses.



### Experimental

The glasses were prepared by mixing together and melting appropriately weighed amounts of the following reagents:  $\text{RbH}_2\text{PO}_4$ ,  $\text{LiCO}_3$ , and  $\text{NH}_4\text{H}_2\text{PO}_4$  for the Rb-Li glasses and  $\text{RbH}_2\text{PO}_4$  and  $\text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5$  for the Rb-Na glasses. All materials were reagent grade and used as received except for  $\text{RbH}_2\text{PO}_4$  which was prepared by reacting  $\text{Rb}_2\text{CO}_3$  with  $\text{H}_3\text{PO}_4$  and dehydrating the product at ca  $150^\circ\text{C}$ . Batches of ca 5 grams were melted in porcelain crucibles in an electric furnace at  $1000^\circ\text{C}$ - $1100^\circ\text{C}$  for 30-45 minutes. The Melts were splat quenched between two stainless steel blocks or poured and allowed to form beads of approximately 0.5 gram. The beads were found to be more convenient for the Raman experiments than the disks obtained by splat quenching but both gave identical spectra. The infrared and Raman spectra of the end member glasses of each series ( $x=0$  and  $x=1$ ) were identical to the spectra of those glasses previously prepared and studied in this laboratory (28,30-32).

The samples for the infrared measurements were prepared by mechanically grinding and dispersing about 10 mg. of glass in 300 mg. of low density polyethylene powder and melting the mixture between two glass plates at ca  $100^\circ\text{C}$  to form clear disks about 3 cm in diameter and 0.03 cm thick. The far infrared spectra were obtained using a Digilab FTS-15 Fourier transform infrared spectrometer with a 6.25 micron mylar beam-splitter. Each spectrum is the result of signal averaging 400 scans at  $2\text{ cm}^{-1}$  resolution.

Raman spectra were obtained on a Jarrell-Ash 25-300 Raman spectrometer using the 488.0 nm line of a Carson argon ion laser at a power of about 500 mW. The spectral accuracy was ca  $1\text{ cm}^{-1}$ . The samples were measured in the form of beads or disks.



### Results

The far infrared spectra of the Rb-Na and Rb-Li glasses, shown in Figures 3 and 4, all contain one strong, broad band centered at about  $460\text{ cm}^{-1}$ . In the spectra of the Rb-Na glasses (Figure 3), the glass containing only Na ( $x=0$ ) exhibits a broad band centered at  $212\text{ cm}^{-1}$  and the Rb glass ( $x=1$ ) exhibits a relatively weak and somewhat sharper band at  $112\text{ cm}^{-1}$ . As  $x$  increases from 0 to 1, both bands are observed in the spectra and their relative intensity varies. The frequencies at which these two bands occur remain constant through the series.

Similar spectra of the Rb-Li glasses are shown in Figure 4. The spectrum of the lithium metaphosphate glass ( $x=0$ ) is apparently featureless and the band analogous to the  $112$  and  $212\text{ cm}^{-1}$  bands observed in the Rb and Na glasses seems to be absent.

The Raman spectra of  $\text{Li}_2\text{O} \cdot \text{P}_2\text{O}_5$  and  $\text{Cs}_2\text{O} \cdot \text{P}_2\text{O}_5$ , which are typical of the spectra of all the metaphosphate glasses reported here, are shown in Figure 5. The Raman spectra of the two series of glasses, Rb-Na and Rb-Li, have been measured at each of several values of  $x$  through each series. The three bands which are of importance in this investigation are those at about  $1260$ ,  $1160$  and  $670\text{ cm}^{-1}$ , which are the asymmetric  $\text{PO}_2$  ( $\omega(\text{PO}_2)_{\text{asym}}$ ), symmetric  $\text{PO}_2$  ( $\omega(\text{PO}_2)_{\text{sym}}$ ) and the symmetric P-O-P ( $\omega(\text{P-O-P})_{\text{sym}}$ ) stretches respectively. The frequencies of the  $\omega(\text{PO}_2)_{\text{sym}}$  and  $\omega(\text{P-O-P})_{\text{sym}}$  bands vary as the composition is varied. The variation of these bands as a function of  $x$ , the mole fraction of Rb, is shown in Figure 6. The  $\omega(\text{PO}_2)_{\text{sym}}$  band has a Lorentzian bandshape whose halfbandwidth decreases systematically with  $x$ , as shown in Figure 7.

## Assignments

### Cation Motion - Far Infrared

In the far infrared spectrum of each single alkali metal metaphosphate glass, there is one band whose frequency depends strongly on the cation. Through a series of  $MPO_3$  glasses it shifts roughly as  $M^{-\frac{1}{2}}$ , where M is the cation mass. This band has been assigned previously (28,31,32) to the cation vibration in its site in the glass and is assumed to be similar to the  $T_{1u}$  mode in an octahedral site. These cation-motion bands occur at 400, 212, 147, 112, and 102  $cm^{-1}$  for Li, Na, K, Rb, and Cs respectively.

In the far infrared spectra of the Rb-Na and Rb-Li mixed alkali glasses shown in Figures 3 and 4, the cation-motion bands for Na (212  $cm^{-1}$ ), and Rb (112  $cm^{-1}$ ) can be seen clearly. As discussed below, these bands vary in intensity as the concentration varies, but the frequencies are essentially unchanged. The Li cation-motion band, which is not apparent here, is very broad and almost totally obscured by absorptions due to the internal network vibrations at about 460  $cm^{-1}$ . The Li cation-motion band in  $LiPO_3(gl)$  has been clearly observed in the emission spectrum, however (28,30).

### Metaphosphate Modes - Raman Spectra

The strong, sharp, polarized band occurring at ca 1160  $cm^{-1}$  in the Raman spectrum of each single alkali metal metaphosphate glass has been assigned previously to the symmetric  $PO_2$  ( $\omega(PO_2)_{sym}$ ) stretching vibration of the "network". The weaker band observed at ca 670  $cm^{-1}$  has been assigned to the symmetric P-O-P ( $\omega(P-O-P)_{sym}$ ) stretching vibration (33,34). Representations of these normal modes of vibration are shown in Figure 9. Both bands are cation dependent and decrease in frequency through the alkali metal metaphosphate series in the order  $Li > Na > K > Rb > Cs$ . In the same order the  $\omega(PO_2)_{sym}$  frequencies are 1172, 1166, 1156, 1152, and 1148 and the  $\omega(P-O-P)_{sym}$  frequencies are 698, 683, 678, 668, and 658 respectively. The  $\omega(PO_2)_{asym}$  band shifts in frequency by only 10  $cm^{-1}$  through the same series.

The Raman spectrum of each of the mixed alkali glasses exhibits the same principal features as those of the single alkali glasses. It is particularly important to note that there

is only one band in the mixed alkali spectra corresponding to each of the  $\omega(\text{PO}_2)$  and  $\omega(\text{P-O-P})$  vibrations of the single alkali glass. Thus, there is, for example, only one  $\omega(\text{PO}_2)_{\text{sym}}$  for any given mixed alkali glass, regardless of the value of  $x$ . Moreover, both the frequency and the half bandwidth of this band vary with  $x$ . As shown in Figure 6, the frequency of the  $\omega(\text{PO}_2)_{\text{sym}}$  band varies systematically and nearly linearly as  $x$  is varied through the composition range of a given mixed alkali series. The variation in half bandwidth is shown in Figure 7. Similarly, there is only one  $\omega(\text{P-O-P})$  band for each mixed alkali glass, and it too varies linearly in frequency as  $x$  is changed. These bands are assigned to the same types of vibrations in the mixed alkali glasses as in the single alkali glasses.

The occurrence of only one, rather than two or more bands for each type of metaphosphate vibration is, of course, a key result. However, the observation of their variation with concentration provides a basis for more detailed structural considerations discussed below.



## Discussion

Metaphosphate Crystal Structure - Before discussing the present results, a brief description of the metaphosphate crystal structure is important to consider. A portion of the crystal structure of  $K_2O \cdot P_2O_5$  ( $KPO_3$ ) is illustrated in Figure 8 (35). This particular fragment contains 4 potassium atoms and segments of 4 different metaphosphate chains. Some of the oxygen atoms along the metaphosphate chains (only those not bound ionically to one of the four potassium atoms in the figure) have been omitted, and the atom sizes have been chosen arbitrarily for the sake of clarity. The metaphosphate chain axes run along the b axis of the crystal which is parallel to and runs down the edge of the figure. Note that potassium atom K1 is bonded to two bridging and six nonbridging oxygens and atom K2 is bonded to one bridging and six nonbridging oxygens. Each potassium atom shares six or seven oxygen atoms with a neighboring potassium atom. Along the phosphate chains, each nonbridging oxygen is bonded to three potassium atoms and each bridging oxygen is bonded to one potassium atom. The crystal structures of  $Rb_2O \cdot P_2O_5$  and  $Na_2O \cdot P_2O_5$  are similar to the  $K_2O \cdot P_2O_5$  structure in that the metaphosphate chain axes are parallel to the b axis and the cations occupy similar sites bonded to six or seven oxygen atoms on three different phosphate chains.

Although the glass has no long range structure, and certainly is different from the crystal in structure, it is expected that the local geometry as well as the forces around each cation and the distribution of cations around each network oxygen are similar in the glassy and crystalline states. This expectation is supported by the observed vibrational spectra of some metaphosphate glasses and their crystalline analogues.

Vibrational Spectra - The far infrared and Raman spectra (30-32) of all of the alkali metal metaphosphate glasses form an envelope of the spectra of the corresponding crystalline material. This



observation provides a strong indication that the short range structure of the glass is similar to that of the corresponding crystal except that the fixed types of sites in the crystal are replaced by a distribution of many types of different but similar sites in the glass. This is consistent with the random network model for the glass structure, in which the local order of the crystal is maintained in the glass, but the long range order is absent. On the basis of these results, it is reasonable to discuss the local vibrations in the glass in terms of the local geometry of the corresponding crystal. The advantage of this approach, of course, is that the structures of the crystalline materials are well known from crystallographic studies, whereas no such detailed structural information is available for glasses.

An examination of the far infrared spectra of the Rb-Na and Rb-Li glasses in Figures 3 and 4 leads to the immediate observations that (1) the intensity of the cation motion band for a particular cation is proportional to the concentration of the cation and (2) the frequency of the cation-motion band for a given cation does not change much as  $x$  varies. This indicates that each cation is in a reasonably well defined site (actually a distribution of sites which are the same as or slightly different from the crystal sites) in the glass and that as the mole fraction of a particular cation varies, the individual cation sites do not change much.

The most important observation concerning the Raman spectra of the mixed alkali glasses is that in each of the three regions where the  $\omega(\text{PO}_2)_{\text{sym}}$ ,  $\omega(\text{PO}_2)_{\text{asym}}$  and  $\omega(\text{P-O-P})_{\text{sym}}$  bands are observed, only one band is present. This is a strong indication that the cations are randomly distributed throughout the glass and that ionic domains (postulated by many authors in connection with mixed alkali effects) are not present. The presence of such ionic domains (regions "rich" in a particular cation) would

require that each  $\omega(\text{PO}_2)\text{sym}$ ,  $\omega(\text{PO}_2)\text{asym}$ , and  $\omega(\text{P-O-P})\text{sym}$  vibration be observed at two or more different frequencies, with each such frequency corresponding to the vibration of the oscillator occurring under the influence of a particular domain environment. That is to say that if there were  $\text{RbPO}_3$  and  $\text{LiPO}_3$  domains in the Rb-Li glasses there would be two  $\omega(\text{PO}_2)\text{sym}$  bands in each, one for each domain, but that is not observed.

Two additional observations of interest in the Raman spectra of the mixed alkali glasses are the systematic variations in (1) the frequencies of the  $\omega(\text{PO}_2)\text{asym}$ ,  $\omega(\text{PO}_2)\text{sym}$ , and  $\omega(\text{P-O-P})\text{sym}$  bands (Figure 6) and (2) the half bandwidths (Figure 7) of the  $\omega(\text{PO}_2)\text{sym}$  band. The fact that the frequencies vary systematically (nearly linearly) as the mole fraction  $x$  is varied can be interpreted as an indication that the  $\text{PO}_2$  vibrational unit is associated with a cation environment which consists of a number of cations, so that its effect on the  $\text{PO}_2$  is an averaged one that changes gradually with cation substitution. The bandwidths are determined by the damping of the vibrational motions. Although the actual damping mechanism involving the  $\text{PO}_2$  vibrational motions is unknown, it is clear from the systematic variation of the half bandwidth of the  $\omega(\text{PO}_2)\text{sym}$  band that the damping is associated with an average cation environment, since it increases in the order (Cs $\rightarrow$ Li) and changes gradually with cation substitution.

The results of an approximate vibrational analysis, discussed below, indicate that the systematic variation in frequency of  $\omega(\text{PO}_2)\text{asym}$  and  $\omega(\text{PO}_2)\text{sym}$  can be accounted for by a systematic decrease in metal-oxygen force constant and increase in  $\text{PO}_2$  bond angle which occur as a large cation is substituted for a smaller one. Similarly, the decrease in  $\omega(\text{P-O-P})\text{sym}$  could be accounted for by an increase in P-O-P bond angle upon substitution of a larger cation for a smaller one, although that is not included in the model considered.

Vibrational Model - The symmetric and asymmetric  $\text{PO}_2$  stretching frequencies  $\omega(\text{PO}_2)\text{sym}$  and  $\omega(\text{PO}_2)\text{asym}$  observed in the Raman spectra of the alkali metal metaphosphate glasses exhibit systematic frequency shifts with cation substitution in both the single alkali glasses and the mixed alkali glasses. The objective of a vibrational

analysis focusing on the  $\text{PO}_2$  unit is to determine what changes accompanying cation substitution might account for these observed frequency shifts. We have designed a model for the  $\text{PO}_2$  vibrational unit which is as simple as possible while still incorporating those parameters which are known to vary systematically with cation (cation mass ( $M_c$ ), M-O force constant ( $F_{m-o}$ ), and  $\text{PO}_2$  bond angle ( $\phi$ )).

Of the several possible models, we have selected the one shown at the bottom of Figure 9, for several reasons. The model indicates that in a given  $\text{PO}_2$  unit the two oxygens are not bonded to a common cation. This is consistent with the crystal structures of the long chain alkali metal metaphosphates (see Figure 8), but it is inconsistent with the crystal structures in that each terminal oxygen is actually bonded to more than one cation (three in  $\text{K}_2\text{O-P}_2\text{O}_5$  for example). A more accurate model would replace the M of our model by a cluster of M's, but for simplicity we have chosen to use the simpler model and to assume that the net effect of the  $M_c$  in our model represents the average effect of a cluster of cations. Another assumption we have made is that the  $\text{PO}_2$  vibrations are independent of the backbone, i.e., localized. This assumption is justified by the observation that the terminal P-O bonds are much stronger than the in-chain P-O bonds and that this is consistent with our assignment of the terminal  $\text{PO}_2$  vibrations to the bands in the  $1100\text{-}1300\text{ cm}^{-1}$  region and of the in-chain vibrations to bands in the  $700\text{-}900\text{ cm}^{-1}$  region. In any case, the effect of the backbone on the  $\text{PO}_2$  vibrations should be largely independent of cation and therefore can be neglected for our purposes.

Our approach to the vibrational analysis with this model was to determine an initial force field which would give good agreement between observed and calculated frequencies for a particular alkali metal metaphosphate glass. Then the dependence of the calculated  $\text{PO}_2$  frequencies on each cation-sensitive



parameter ( $F_{m-o}$ ;  $F_{p-o}$ ;  $M_c$ ; and  $\phi_{o-p-o}$ ) was investigated. It was found that the two parameters which caused the most significant change in frequencies were  $F_{m-o}$  and  $\phi$ . The  $\omega(PO_2)_{sym}$  and  $\omega(PO_2)_{asym}$  frequencies are essentially independent (effects less than  $1\text{ cm}^{-1}$ ) of cation mass for  $M_c > 4\text{ amu}$ . The frequencies are also dependent on  $F_{p-o, m-o}$  although the total contribution from this parameter was found to be less than  $2\text{ cm}^{-1}$  for  $F_{p-o, m-o} < .05 \times 10^5\text{ dyne/cm}$ . The dependences of  $\omega(PO_2)_{sym}$  and  $\omega(PO_2)_{asym}$  on the two most significant parameters,  $F_{m-o}$  and  $\phi$ , are shown in Figure 10.

These results are encouraging for three reasons. First, it is known from crystallographic studies that the terminal  $PO_2$  bond angle increases through the series of alkali metal metaphosphate ( $117^\circ$  for Na to  $120^\circ$  for Rb). Secondly, the force constants,  $F_{m-o}$  decrease in going through the same series and they have been determined previously from the cation-motion bands in the far infrared spectra. Finally, these trends observed in  $\phi$  and  $F_{m-o}$  are qualitatively consistent with the observed variations in the  $\omega(PO_2)_{asym}$  and  $\omega(PO_2)_{sym}$  vibrational frequencies. Thus, as  $\phi$  increases and  $F_{m-o}$  decreases through the series of alkali metals (Li-Cs), the calculated  $\omega(PO_2)_{sym}$  is decreased by both parameters while the calculated  $\omega(PO_2)_{asym}$  is decreased by  $F_{m-o}$  and increased by  $\phi$ . Such a result is consistent with the observation that  $\omega(PO_2)_{sym}$  decreases by  $24\text{ cm}^{-1}$  and  $\omega(PO_2)_{asym}$  decreases by only  $10\text{ cm}^{-1}$ .

In order to make these qualitative observations more quantitative, the initial force field was used as a basis for calculating the vibrational frequencies of the series of alkali metal metaphosphates. The only parameters varied throughout the series were  $F_{m-o}$ ,  $\phi$ , and  $M_c$ ; all other force field elements and structural parameters were held constant. The metal-oxygen force constants ( $F_{m-o}$ ) were taken to be twice the  $F_{T_{1u}}$  force constants determined previously from the cation motion bands in the far



infrared and the cation masses were not adjustable so that the only adjustable parameter was  $\phi$ , the O-P-O bond angle. Although  $\phi$  is an adjustable parameter, the values used for it are reasonable and nearly the same as in the crystalline analogues. The final force field and structural parameters are shown in Table I, and the observed and calculated frequencies are given in Table II. Note that the  $\omega(\text{PO}_2)_{\text{sym}}$  and  $\omega(\text{PO}_2)_{\text{asym}}$  bands and the calculated M-O stretching and  $\text{PO}_2$  bending frequencies are in good agreement with the observed frequencies. The results are quite good considering the assumptions of the model and the fact that only one adjustable parameter was used.

These results can be further extended to explain the systematic variation of  $\omega(\text{PO}_2)_{\text{sym}}$  and  $\omega(\text{PO}_2)_{\text{asym}}$  with composition in a series of mixed alkali glasses. Recall that the cation mass in our model is considered to represent the average effect of a "cluster" (perhaps 3) of cations. If we assume that the three parameters ( $F_{\text{m-o}}$ ,  $\phi$ , and  $M_c$ ) vary systematically with cation substitution in a series of mixed alkali glasses, then we should expect to observe a similar systematic variation in  $\omega(\text{PO}_2)_{\text{sym}}$  and  $\omega(\text{PO}_2)_{\text{asym}}$ . Such a systematic variation in M can be explained by a random substitution process in which the introduction of a cation M' into an  $\text{M}_2\text{O} \cdot \text{P}_2\text{O}_5$  glass results in the replacement of an M by an M' in a random fashion. If the substitution process is not random and domains rich in a particular cation are formed, one would expect to find more than one band corresponding to  $\omega(\text{PO}_2)_{\text{sym}}$  or  $\omega(\text{PO}_2)_{\text{asym}}$ , each band resulting from the vibrations of  $\text{PO}_2$  units associated with predominantly M or M'. The extension of this vibrational model to mixed alkali glasses is made with some reservation and is certainly not to be taken as a quantitative explanation.

### Summary and Conclusions

The infrared and Raman spectra of two series of mixed alkali glasses provide evidence that: 1) the cations are homogeneously distributed (no domain formation), 2) the vibrationally significant local geometry and forces associated with a particular cation are unaffected by the introduction of the second cation into the glass structure, and 3) the phosphate chains are associated with an average cation environment which changes gradually with the mole fraction of a particular cation in a series of mixed alkali glasses.

A vibrational analysis of a  $\text{PO}_2$  model indicates that the observed frequency shifts in the  $\text{PO}_2$  vibrational bands may be a natural consequence of the increase in  $\text{PO}_2$  bond angle and decrease in metal oxygen force constant resulting from substitution of a larger cation for a smaller one.

### Acknowledgment

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TABLE I

Cation	$F_{P-O}$	$F_{M-O}$	$F_{O-P-O}$	$F_{P-O,P-O}$	$M_c$	$r_{P-O}$	$\phi_{O-P-O}$
Li	9.1	.55	.42	.62	6.9	1.47	114.5
Na	9.1	.37	.42	.62	23.	1.47	118.
K	9.1	.24	.42	.62	39.	1.47	119.
Rb	9.1	.19	.42	.62	85.5	1.47	120.
Cs	9.1	.16	.42	.62	133.	1.47	120.

All force constant units are  $10^5$  dyne  $\text{cm}^{-1}$ .  $F_{O-P-O}$  has been converted to these units by dividing by  $r_{P-O}^2$ . Masses and bond lengths are in units of amu and Å, respectively.



TABLE II

Cation	$\omega(\text{PO}_2)\text{asym}$		$\omega(\text{PO}_2)\text{sym}$		$\omega(\text{M-O})$		$\omega(\text{O-P-O})$	
	obs	calc	obs	calc	obs	calc	obs	calc
Li	1260	1262	1172	1186	400	396	a	335
Na	1268	1267	1166	1167	212	209	a	380
K	1270	1267	1156	1158	147	146	a	378
Rb	1268	1268	1152	1152	112	112	a	378
Cs	1270	1268	1148	1151	95	97	a	378

a. It is difficult to assign a particular frequency to this mode.

The Raman spectra contain a weak, broad feature centered at about  $350 \text{ cm}^{-1}$ .

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# Figure Captions

Figure 1. Physical properties of mixed alkali glasses as a function of mole fraction of a particular cation.

- a) Refractive index vs. mole fraction K for the system  $xK_2O \cdot (1-x)Na_2O \cdot SiO_2$ . (9).
- b) Density ( $g\ cm^{-3}$ ) vs. mole fraction K for the system  $xK_2O \cdot (1-x)Na_2O \cdot SiO_2$ . (9).
- c) Molar volume ( $cm^3\ mole^{-1}$ ) vs. mole fraction K for the system  $xK_2O \cdot (1-x)Na_2O \cdot SiO_2$ . (9).
- d) Log viscosity (poise) vs. mole fraction K for the system  $xK_2O \cdot (1-x)Na_2O \cdot 3.16\ SiO_2$  ( $500^\circ C$ ) (1,10).
- e) Glass transition temperature ( $T_g$ ,  $^\circ C$ ) vs. mole fraction K for the system  $xK_2O \cdot (1-x)Na_2O \cdot 5.55SiO_2$ . (1,11).
- f) Thermal expansion coefficient ( $\alpha \times 10^6$ ) vs. mole fraction K for the system  $xK_2O \cdot (1-x)Na_2O \cdot 5.55\ SiO_2$ . (1,11).

Figure 2. Physical properties of mixed alkali glasses as a function of mole fraction of a particular cation.

- a)  $\tan \delta \times 10^4$  at  $1.5 \times 10^6$  Hz and  $20^\circ C$  vs. mole fraction K for the system  $xK_2O \cdot (1-x)Na_2O$ , .14 ca  $F_z$ , .32 PbO, 1.66  $SiO_2$ . (12).
- b) Dielectric loss factor ( $\log \epsilon''$ ) at 1 KHz vs. mole fraction Cs for the system  $xCs_2O \cdot (1-x)Na_2O \cdot 5SiO_2$  (upper curve at  $260^\circ C$ , lower curve at  $120^\circ C$ ). (13)
- c) Activation energy ( $Kcal\ mole^{-1}$ ) for ionic conductivity vs. mole fraction Cs for the system  $xCs_2O \cdot (1-x)Na_2O \cdot 5\ SiO_2$ . (13)

- d) Log conductivity ( $\text{ohm}^{-1}\text{cm}^{-1}$ ) vs. mole fraction Cs for the system  $x\text{Cs}_2\text{O} \cdot (1-x)\text{Na}_2\text{O} \cdot 5\text{SiO}_2$ , (13).

Figure 3. Far infrared spectra of glasses in the series  $x\text{Rb}_2\text{O} \cdot (1-x)\text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5$ .

Figure 4. Far infrared spectra of glasses in the series  $x\text{Rb}_2\text{O} \cdot (1-x)\text{Li}_2\text{O} \cdot \text{P}_2\text{O}_5$ .

Figure 5. Raman spectra of  $\text{Li}_2\text{O} \cdot \text{P}_2\text{O}_5$  and  $\text{Cs}_2\text{O} \cdot \text{P}_2\text{O}_5$ .

Figure 6. The systematic variation in frequency of the  $\text{PO}_2$  stretching vibrations vs. mole fraction Rb for the two systems  $x\text{Rb}_2\text{O} \cdot (1-x)\text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5$  (circles) and  $x\text{Rb}_2\text{O} \cdot (1-x)\text{Li}_2\text{O} \cdot \text{P}_2\text{O}_5$  (plusses),

Figure 7. The half bandwidths of the  $\text{PO}_2$  symmetric stretching peak vs. mole fraction Rb for the two systems  $x\text{Rb}_2\text{O} \cdot (1-x)\text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5$  (circles) and  $x\text{Rb}_2\text{O} \cdot (1-x)\text{Li}_2\text{O} \cdot \text{P}_2\text{O}_5$  (plusses).

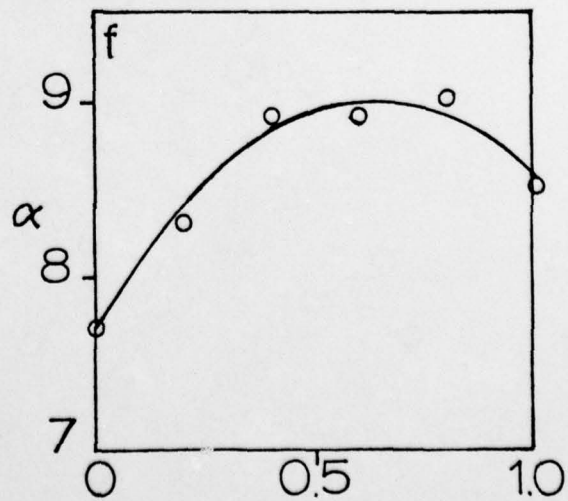
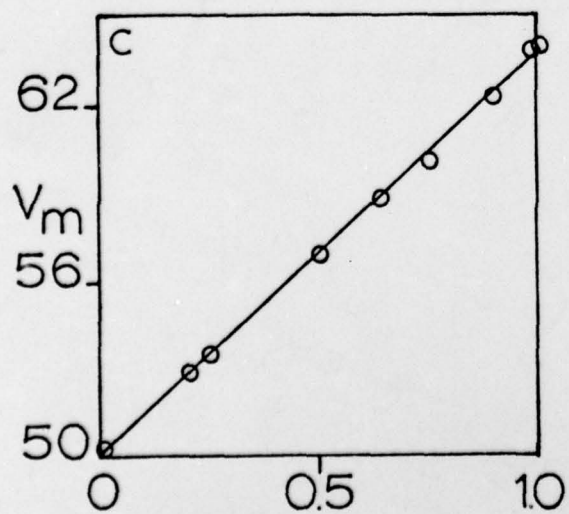
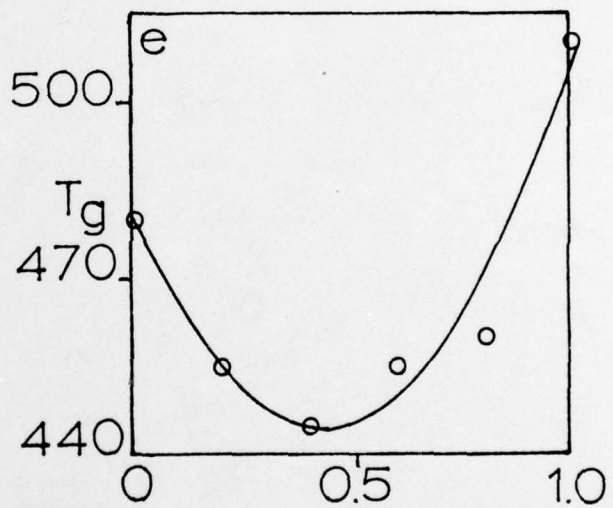
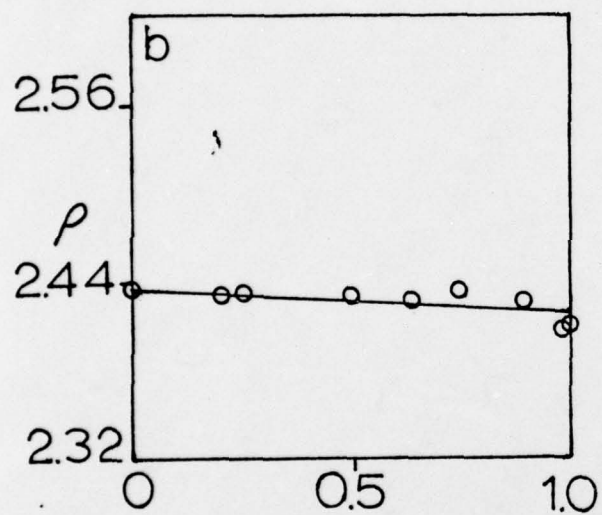
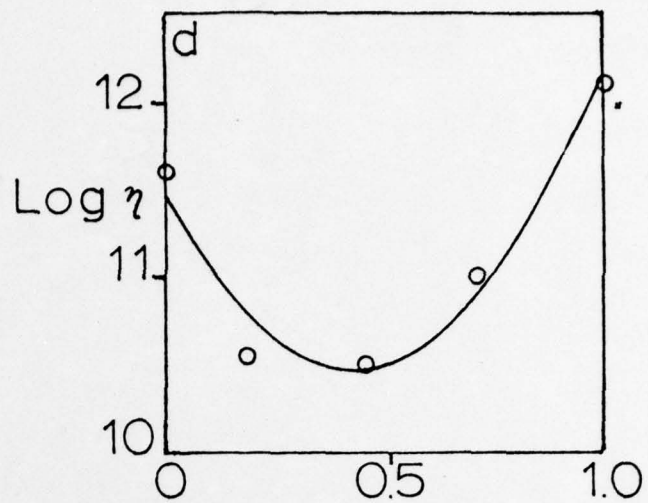
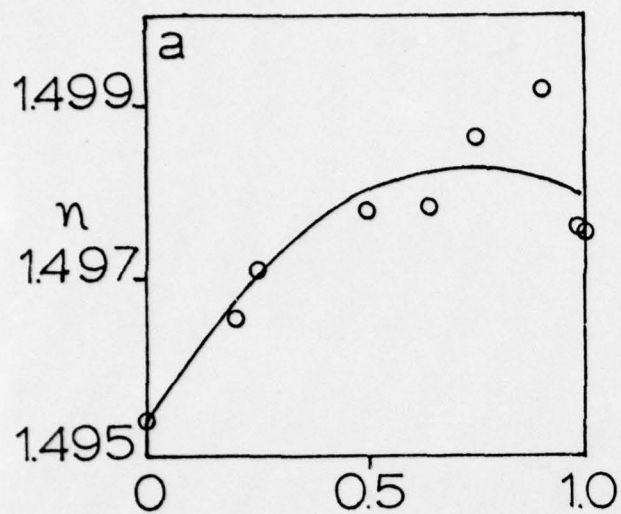
Figure 8. A fragment of the  $(\text{KPO}_3)_x$  crystal structure (referred to as  $\text{K}_2\text{O} \cdot \text{P}_2\text{O}_5$  in the text). The circles labelled K1 and K2 represent potassium atoms, the smallest circles represent phosphorous atoms, and the other circles represent oxygen atoms.

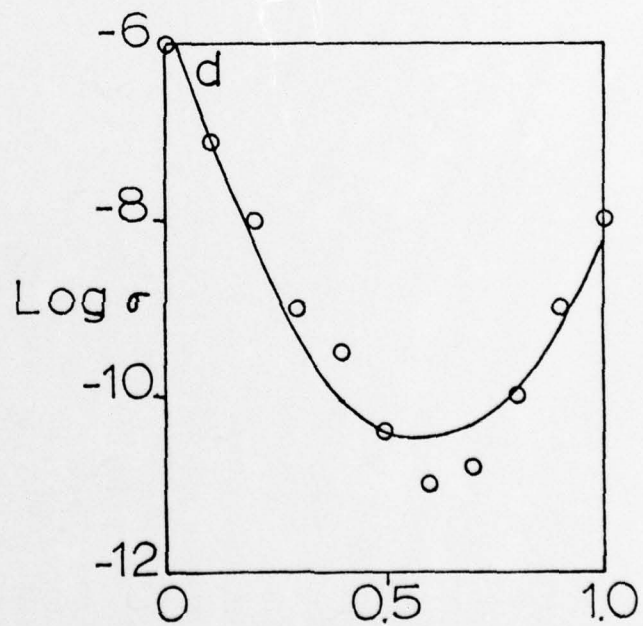
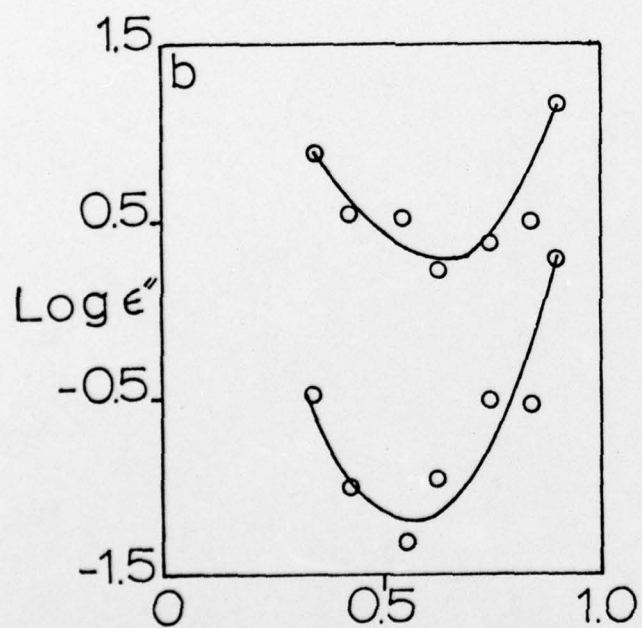
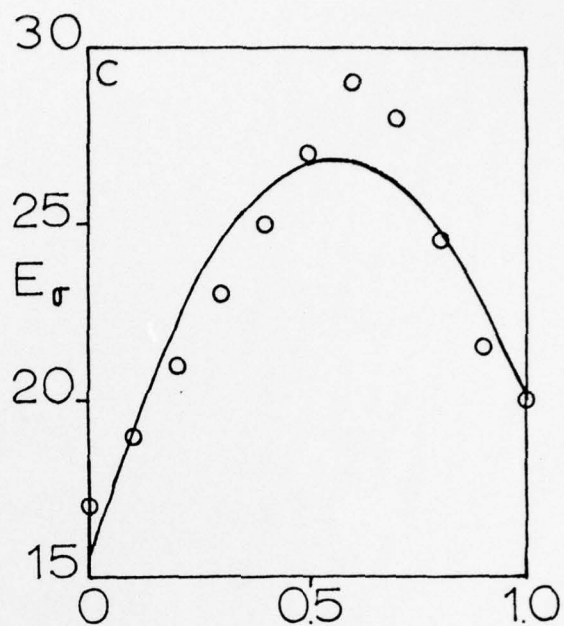
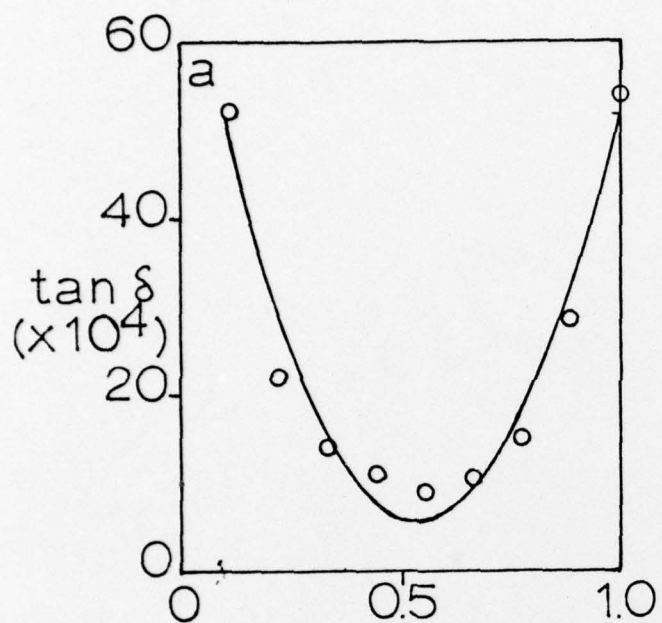
Figure 9. The upper four figures represent the normal modes of vibration of the phosphate chain and the terminal  $\text{PO}_2$  vibrations

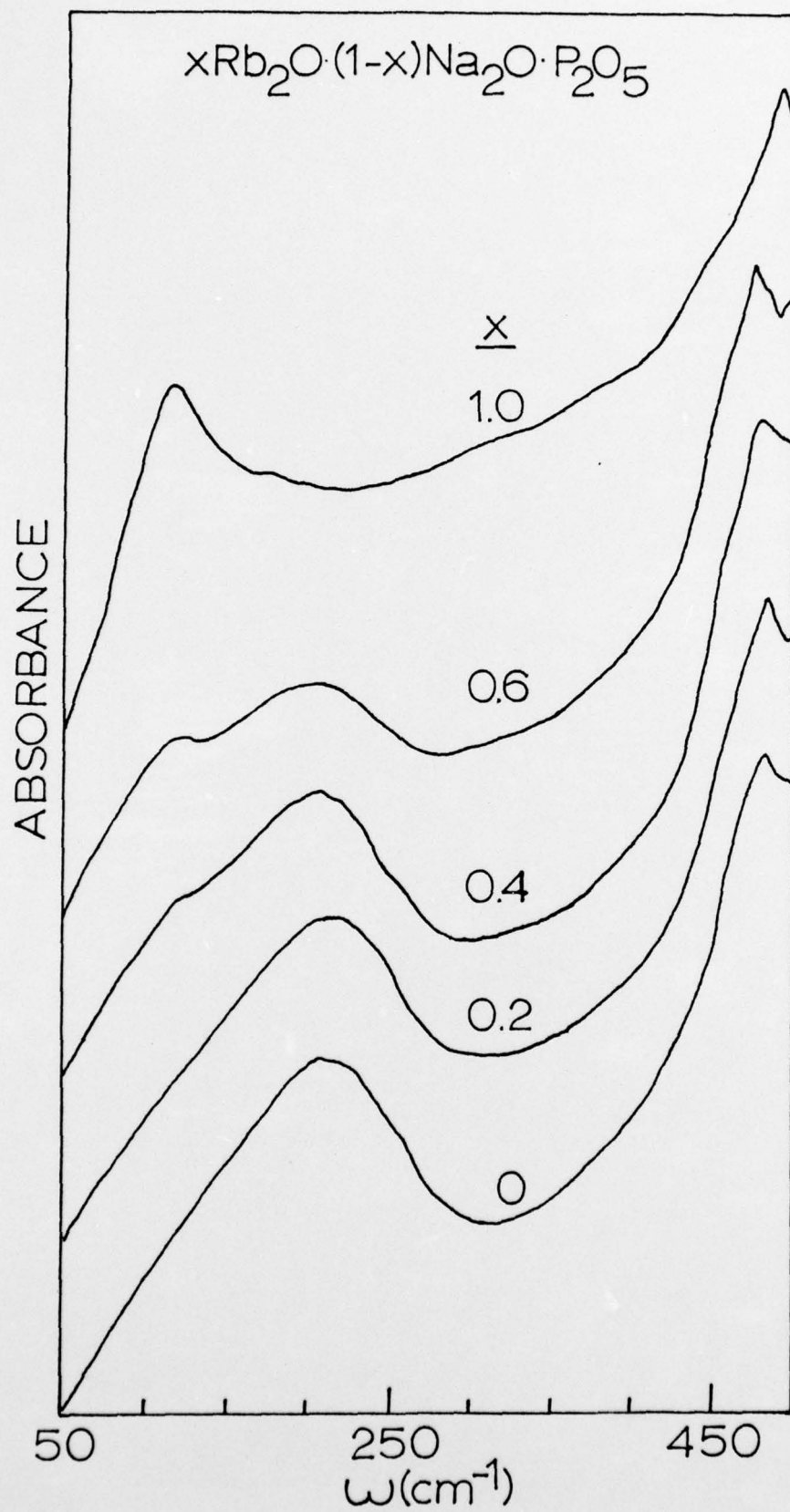
discussed in the text. The letters C and S represent bond closing and bond opening respectively. The figure at the bottom represents the model for the terminal  $\text{PO}_2$  vibrational unit used with calculations.

Figure 10. The dependence of calculated  $\text{PO}_2$  stretching vibrations on the two parameters  $F_{\text{M-O}}$  (represented by plusses) and  $\phi$  (represented by circles). For the curves representing the dependence on  $F_{\text{M-O}}$ , the values of the other parameters were held constant at  $F_{\text{P-O}} = 9.1$ ,  $F_{\text{OPO}} = .42$ ,  $F_{\text{P-O,P-O}} = .55$ ,  $M_c = 23$  and  $\phi = 115$ . For the curves representing the dependence on  $\phi$ , the other parameters were held constant at  $F_{\text{P-O}} = 9.1$ ,  $F_{\text{M-O}} = .37$ ,  $F_{\text{OPO}} = .42$ ,  $F_{\text{PO,PO}} = .55$ , and  $M_c = 23$ .

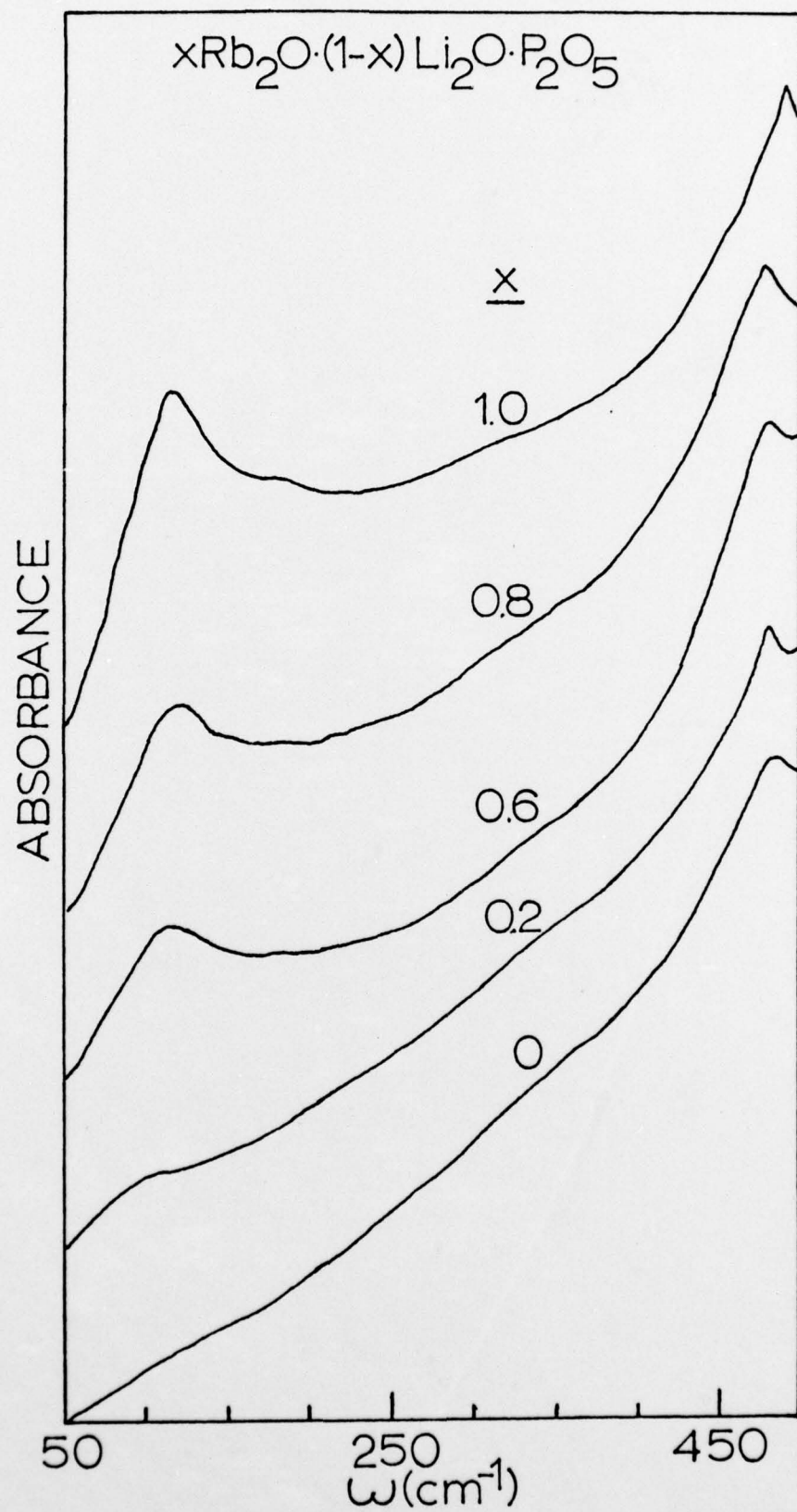


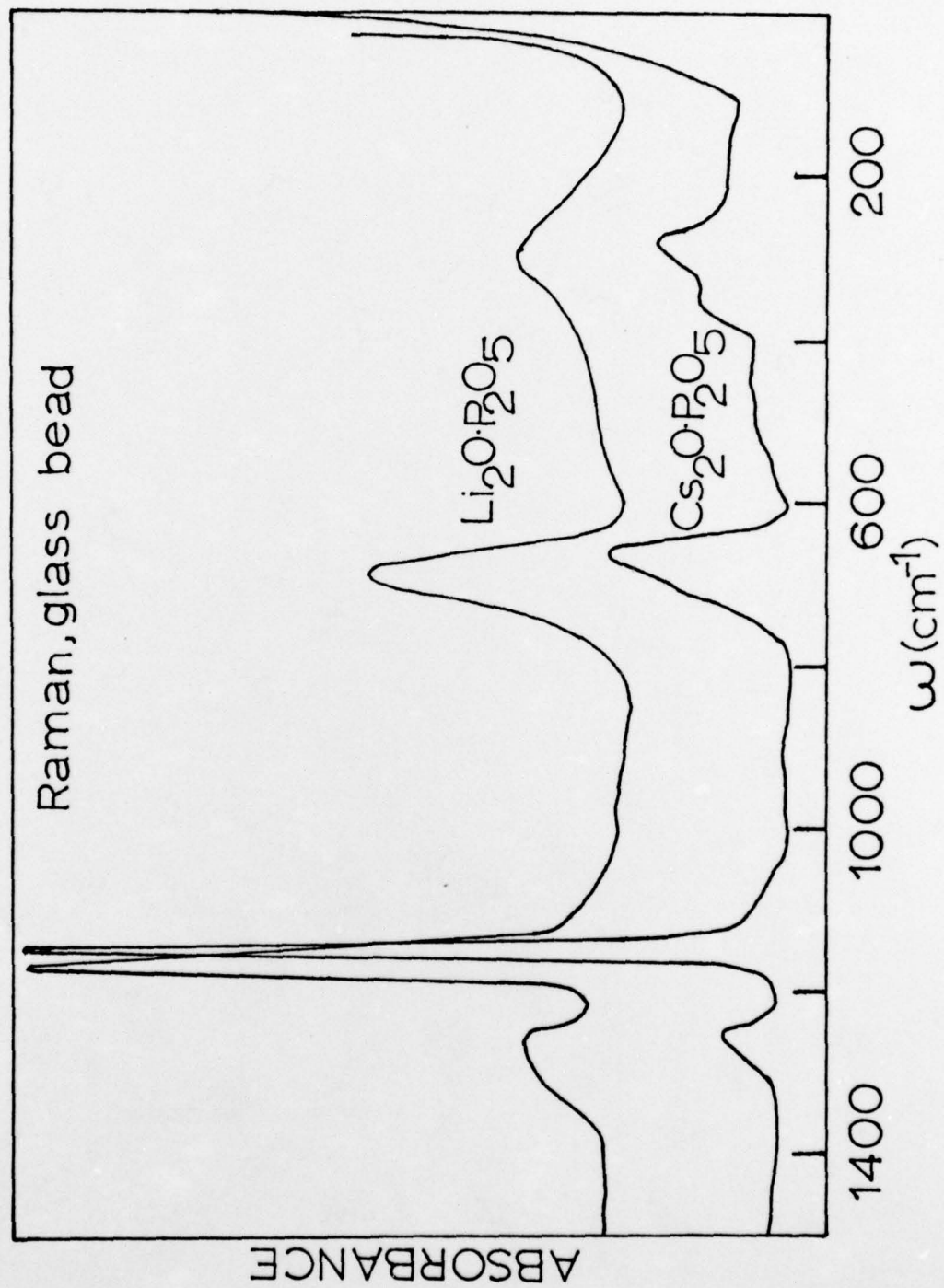


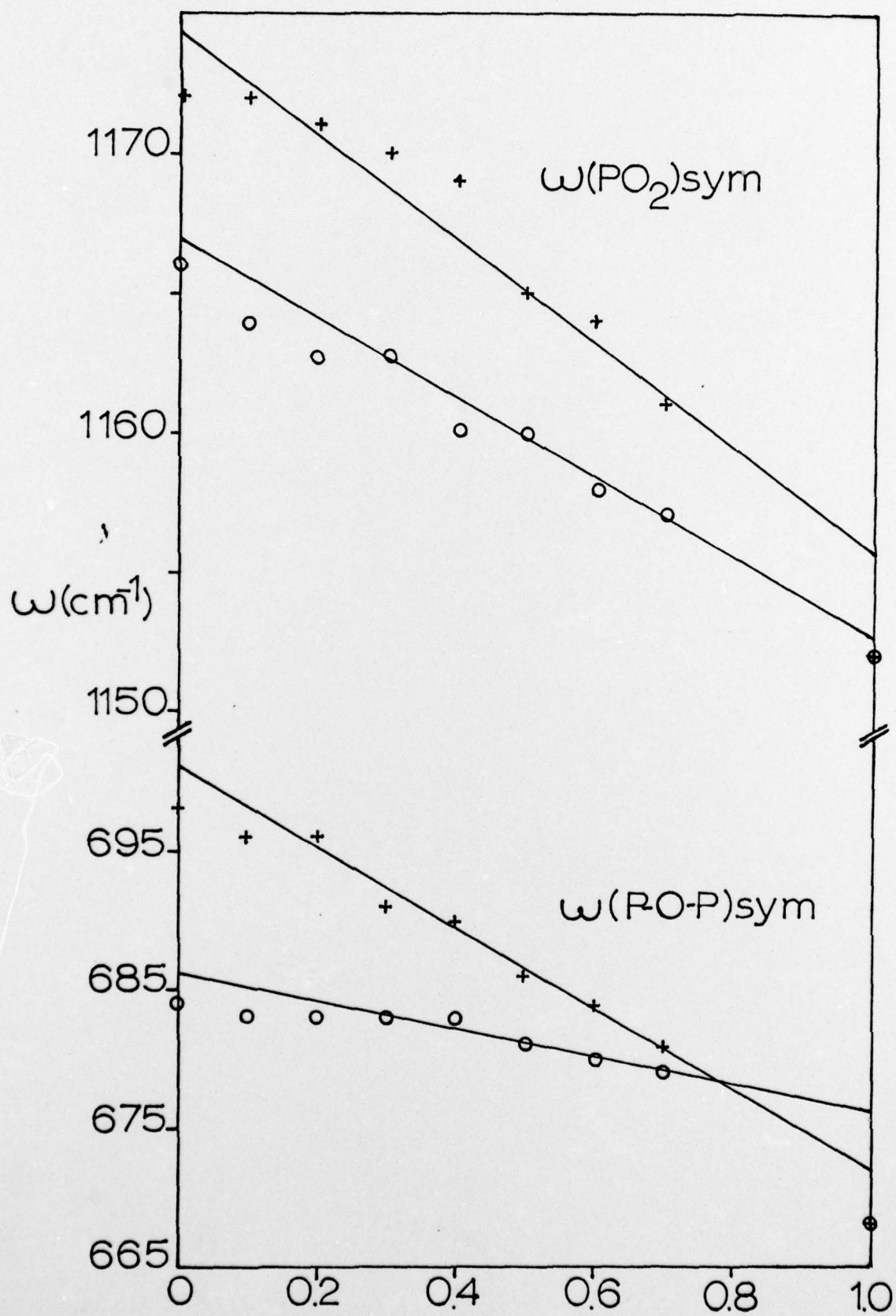




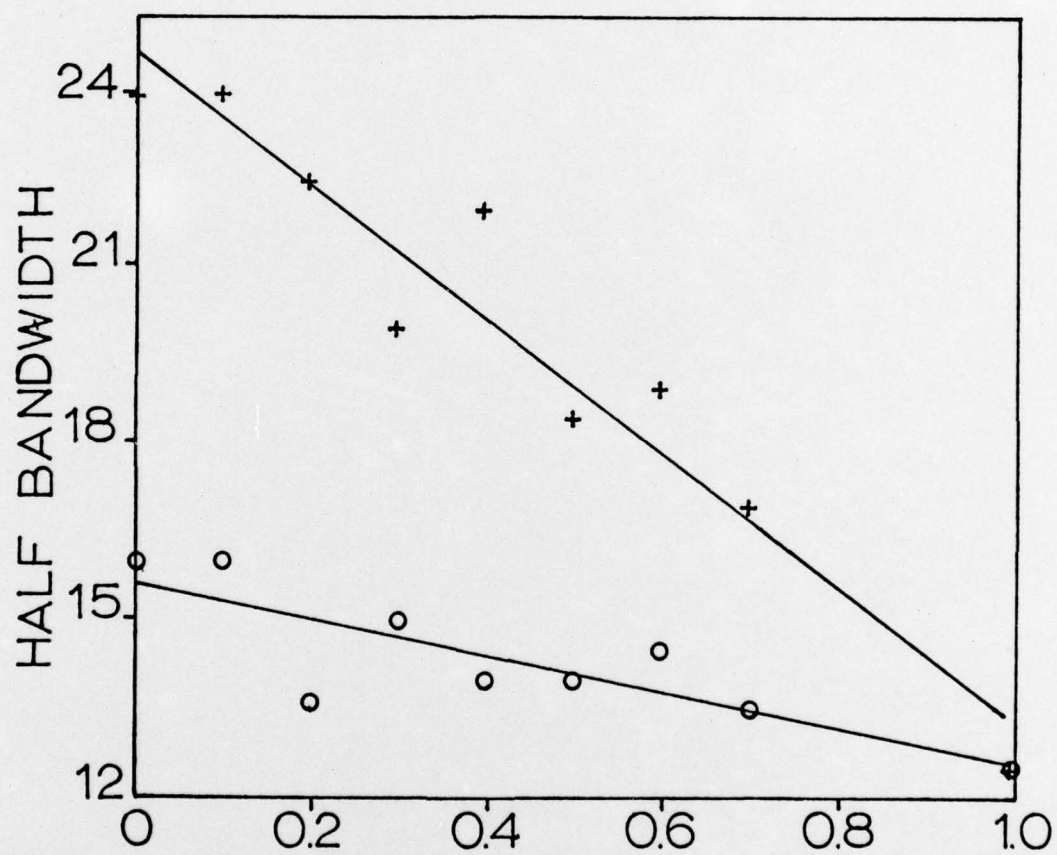


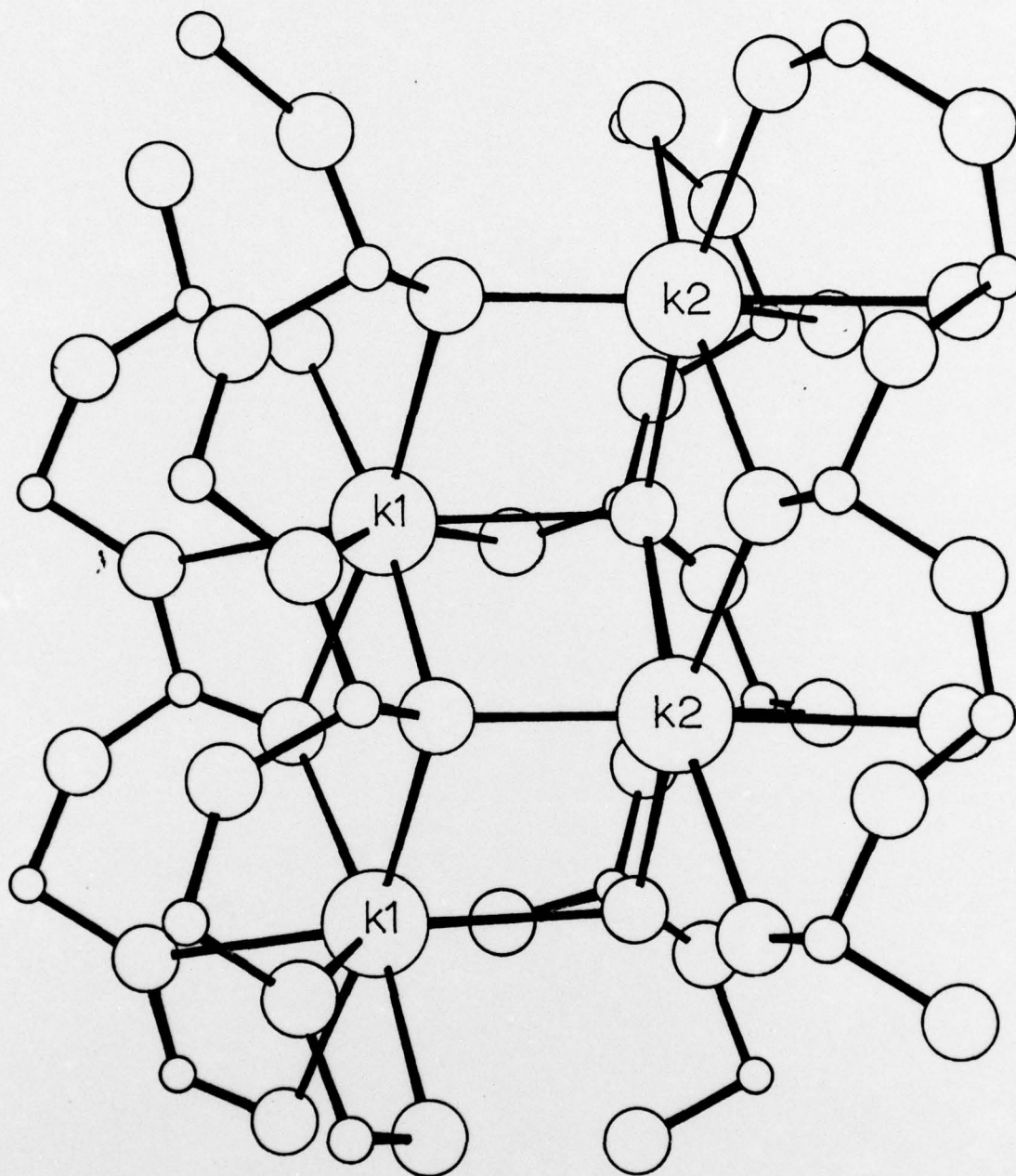


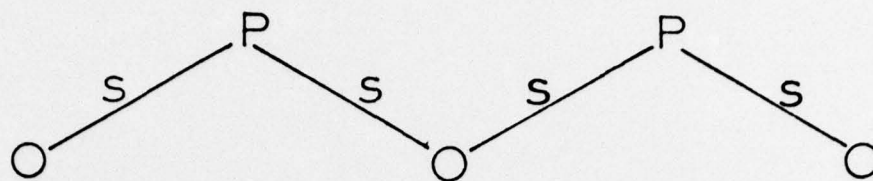




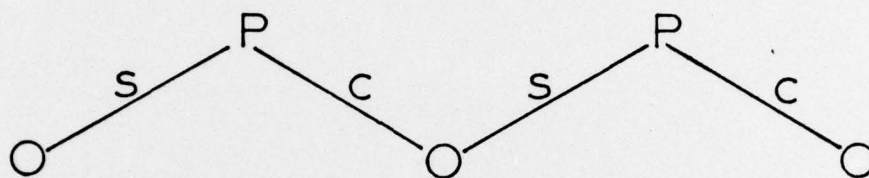




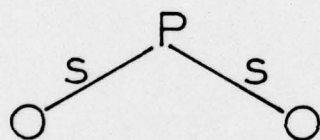




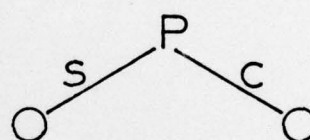
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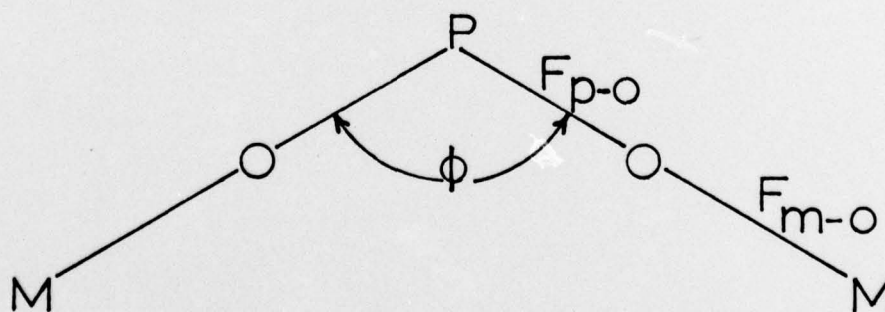
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Symmetric  $\text{PO}_2$  Stretch

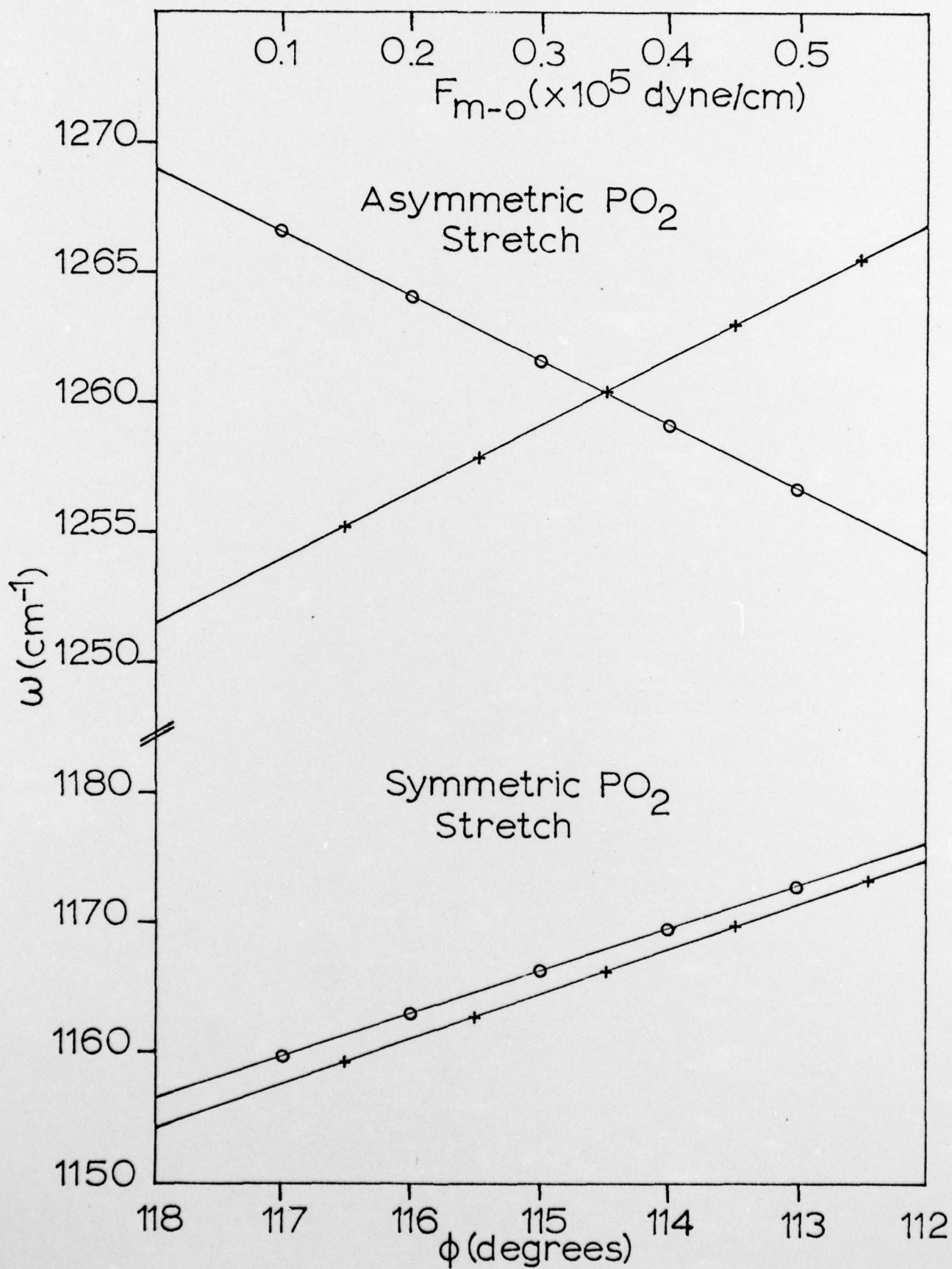


Asymmetric  $\text{PO}_2$  Stretch



$\text{PO}_2$  Vibrational Model





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